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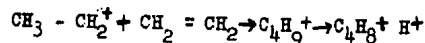
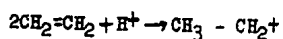
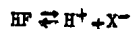
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THE PROTON-ION MECHANISM OF ALKYLATION
 AND POLYMERIZATION REACTIONS

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 T. P. Vishnyakova, and M. V. Kurashov

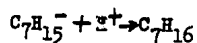
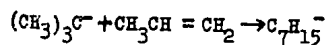
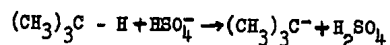
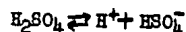
According to the theory of acid catalysis, the reaction mechanism of alkylation and polymerization is based on the ability of the acid to transfer protons and electrons.

The theory of proton-ion polymerization proposed by Whitmore (1) in 1934 is based on the fact that an acid proton becomes attached to the olefinic double bond, forming a charged radical - the carbonium ion which initiates the polymerization reactions:



The carbonium ion theory was widely accepted and applied to alkylation.

The alkylation reaction mechanism proposed by Ciapetta (2) is based on the following: because of the action of the acid, a proton and an electron split off from isobutane, which becomes a charged radical or carbonium ion. The carbonium ion then attaches itself to the olefinic double bond:



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Many mechanisms for the alkylation reaction with the carbonium ion exist, among which there is little difference (3).

The present work undertakes to check the proton-ion mechanism for the reactions of alkylation and polymerization.

The authors started with the assumption that if the catalysis is brought about by the protons or ions of the acid, then a connection between electrical conductivity and catalytic activity must exist. Electrical conductivity is produced by the ion concentration, and therefore, the greater this concentration the greater the catalytic activity of the acid, since the ions catalyze the reaction.

This relationship is observed only with anhydrous acids, since hydrated ions are catalytically less active.

The conductivity, at unit potential, is directly related to the ion concentration:

$$x = c(U+V)$$

where x is conductivity, i. e. the value equal to the reciprocal resistance of one ml of electrolyte; U and V are mobilities of the ions, which represents the products of the velocity of ions and of their charge. The following are the absolute values of the velocities and mobilities of the ions:

<u>Ion</u>	<u>Velocity</u> (cm/sec)	<u>Mobility</u> (Coul x cm/sec)
H ⁺	0.000324	313
F ⁻	0.00048	46.6
$\frac{1}{2}\text{SO}_4^{--}$	0.00070	67.9

In studying the proton-ion reaction mechanism, the conductivities of a series of anhydrous acids, well known as catalysts, were determined, and an attempt was made to establish the relationship between catalytic activity and conductivity.

The conductivity was determined in the usual manner: 5 - 6 ml of the electrolyte were placed in a small beaker with platinum electrodes; the beaker was then placed in a constant temperature device, and the resistivity was measured with the aid of a resistance bridge and an audiogenerator. The conductivity was found from the relationship:

$$x = C/R$$

where C is the volume of the beaker, R is resistivity.

In Table 1 are listed the properties of catalysts whose conductivities were determined.

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Table 1. Characteristics of the Catalysts (4)

Compound	Sp Gr	Bp	Amt. BF ₃ (%)
H ₃ PO ₄ ·BF ₃	1.90	decomp	41.0
H ₄ P ₂ O ₇ ·2BF ₃	--	--	43.4
H ₂ O·BF ₃	1.77 (15°)	decomp	79.0
BF ₃ ·2H ₂ O	1.62 (20°)	58 - 60 (1 mm)	65.4
CH ₃ OH·BF ₃	1.41	decomp	--
C ₂ H ₅ OH·BF ₃	1.35	decomp	--
C ₆ H ₅ OH·BF ₃	1.24	decomp	--
H ₂ SO ₄ + BF ₃	1.84	--	--
(C ₂ H ₅) ₂ O·BF ₃	1.135 (13°)	126 - 127	47.2
H ₃ PO ₄	1.88	--	--

The compounds in Table 1 are strong acids and represent catalysts for polymerization and alkylation.

Below are listed the conductivity values of a series of acid catalysts and their characteristics in reactions of polymerization and alkylation.

Table 2. Characteristics of Conductivity and Catalytic Activity of Catalysts

(A plus sign indicates that the reaction takes place, while a zero indicates the absence of a reaction)

Catalyst	Conductivity at 25° 1 cm ⁻¹			Alkylation of Isobutane			Polymerization at Atm Pressure and 100°		
	Specific	Equi- valent	Mol- ar	C ₃ H ₄	C ₃ H ₆	C ₄ H ₈	C ₂ H ₄	C ₃ H ₆	1-C ₄ H ₈
HF	-	-	-	0	+	+	0	+	+
H ₄ PO ₄ ·BF ₃	0.00722	0.205	0.15	+	+	+	weak	+	+
H ₄ P ₂ O ₇ ·2BF ₃	0.0067	0.27	1.08	+	+	+	weak	+	+
H ₂ O·BF ₃	0.0386	0.94	1.88	+	+	+	-	+	+
BF ₃ ·2H ₂ O	0.1660	-	-	0	0	0	0	0	+

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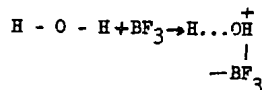
Catalyst	Specific	Equi- valent	Mol- ar	C ₃ H ₄	C ₃ H ₆	C ₄ H ₈	C ₂ H ₄	C ₃ H ₆	1-C ₄ H ₈
CH ₃ OH·BF ₃	0.01371	0.966		0	weak +	-	-	-	-
C ₂ H ₅ OH·BF ₃	0.00854	0.718		0	weak +	0	-	-	-
C ₆ H ₅ OH·BF ₃	0.000528	-		0	0	0	0	+	+
(C ₂ H ₅) ₂ O·BF ₃	0.0028	0.350		0	0	0	0	0	+
H ₂ SO ₄ +BF ₃	0.0356	-	-	+	+	+	-	+	+
H ₂ SO ₄	0.0435	1.158	2.316	0	weak +	0	weak	+	+
H ₃ PO ₄	0.0510	0.885	2.66	0	0	0	0	0	+

The data on alkylation and polymerization reactions in Table 2 represent results of our prior work.(5) The alkylation reaction was carried out in the liquid phase while the polymerization reaction was conducted by passing the gaseous olefin through a column, the filling of which consisted of moistened catalyst. The results of the conductivity determination in Table 2 show that no correlation exists between the conductivities (and hence the concentration of the active electrolyte ions) and the catalytic activity.

The most active catalysts, such as H₃PO₄·BF₃ and H₄P₂O₇·2BF₃, which bring about alkylation of isoparaffins with ethylene, propylene, and butylene, and are also the most energetic in polymerization reactions, have a lower conductivity (0.0072 and 0.0067 Ω⁻¹cm⁻¹) than sulfuric or phosphoric acids (0.0435 and 0.0510 Ω⁻¹cm⁻¹).

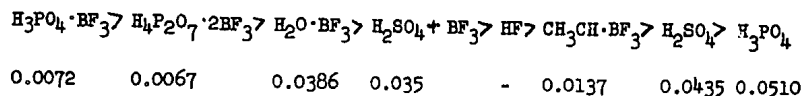
If the proton-ion theory of catalysis were true, one could expect the opposite.

Another fact which deserves attention is that the conductivities of phosphoric and sulfuric acids are lowered when they are saturated with BF₃. This is especially noticeable with orthophosphoric acid. At the same time, the catalytic activity of the compounds of BF₃ with the acids is increased. The increase in polarity during the change from acid to acid compound with BF₃ lowers the degree of electrolytic dissociation. Molecular compounds of boron fluoride with water or alcohols (6) acquire the character of strong acids in connection with the fact that the hydrogen bond of hydroxyl groups in molecular compounds becomes ionic.



In ether adducts of boron fluoride there are no hydroxyl groups and the compounds do not have an acidic character.

It was shown in one of our papers (6) that catalysts of alkylation and polymerization can be arranged in the order of decreasing activity as follows:



(In the second line are the respective conductivities).

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This illustrates at a glance the lack of a connection between conductivity (ion concentration in anhydrous electrolytes) and ions' catalytic activity. In other words, experimental data contradict the theory of proton-ion mechanism.

On the basis of what has been stated, it can be concluded that the catalytic action of acids in alkylation and polymerization reactions is not connected with the ion concentration of the acids and therefore with the formation of carbonium ions. However, this action apparently can be explained by a complex-forming mechanism similar to that which operates in the case of aluminum chloride, since strong acids have a clearly defined polar character and hence have a tendency to form complexes.

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